Characteristics and Mechanism of Thermal Ion Emission from Negative Ion Beam Source using Solid Ionic Conductors

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論文内容要旨

Negative ion beams have a high potential in material processing such as ion beam implantation and ion beam machining, because of their “nearly charge-up free” feature in ion beam irradiation. Despite this advantage, negative ion beams have not been widely used yet. One of the major reasons is that the efficient production of negative ion beams is not easy by a conventional discharge plasma method.

So far, the author and co-workers have proposed an O^- ion production method by utilizing solid oxide ionic conductors. And, until now, the O^- ion emission from this novel negative ion beam source has been investigated in not only our previous works, but also other works by several groups. However, the performance of this negative ion beam source is not enough for practical use, and its emission mechanism have not been clarified well. In addition, the variations of the works are too narrow: All of these are the works related to the ion emission from Yttria Stabilized Zirconia (YSZ) or $12CaO{\cdot}7Al_2O_3$ (C12A7). For the upgrading of the performance, the exploring of the additional potentiality and the clarification of the mechanism of this ion beam source, the author has considered that it is essential to develop this study from various perspectives using various materials.

Therefore, in this dissertation, the first, the purpose is to investigate the O^- ion emission from the oxide ionic conductor other than YSZ and C12A7, to find a new candidate material for the performance upgrading. Next, to seek the additional potentiality, trial will be made for the productions of the negative ion beam other than O^- ion using other ionic conductor. And finally, the author aims to clarify the emission mechanism using the obtained data from these experiments.

Emission characteristics of O^- ion from CeO_2 were investigated to find a new candidate material for the performance upgrading of the O^- ion beam source. The quadrupole mass spectrum obtained from CeO_2 was shown in Fig. 1. It was confirmed that negative ions emitted CeO_2 were mainly O^- ions. This result proved that it is possible to produce O^- ion beam by using CeO_2 other than YSZ and C12A7. In addition, the emission current from CeO_2 was also observed. It was found that the emission current decreases with the passage of time. However, the tendency of the decay curves at each temperature varies widely. A possible reason for the variation in the tendency is that the condition of the emission surface was different among the samples used at each temperature. It was also found that the emission current increases with temperature. And, additionally it was found that the emission current increased with applied voltage.

The emission current from CeO_2 was higher than that from YSZ and C12A7 in a low voltage region, suggesting that it is possible to increase the emission current by using an oxide ionic conductor other than YSZ and C12A7.

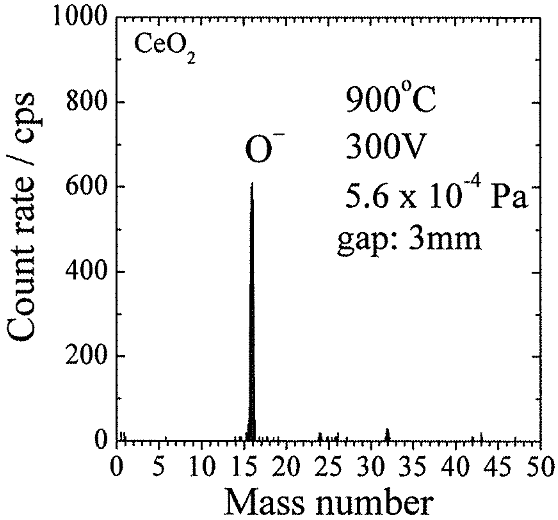

Fig. 1 Mass spectrum of negative ions from CeO_2 at 900°C under the extraction voltage of 300V

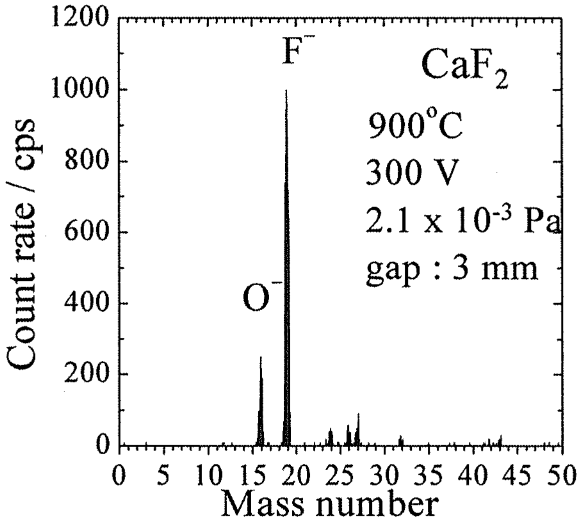

Fig. 2 Mass spectrum of negative ions from CaF_2 at 900°C under the extraction voltage of 300V

To explore the additional potentiality of this system, F^- ion emission from CaF_2 was investigated. As shown in Fig. 2, the production of F^- ion from CaF_2 was confirmed by the quadrupole mass spectrometry, indicating that this system can produce the F^- ion beam by using fluoride ionic conductor. However, a certain amount of O^- ion was also contained in the emitted negative ions. This is because that the emission surface of the sample was oxidized during the sintering procedure of the Pt electrode.

In addition, the emission current from CaF_2 was also observed. It was found that the emission current showed the similar decay behavior, which was often observed in the O^- ion emission from oxide ionic conductors: The emission current shows a rapid decay at initial stage, and then, it decreases gradually with the passage of time. It should be considered that the decay behavior of the emission current is specific phenomenon in ion emissions from a solid surface. It was also found that the emission current increases with temperature. The activation energy for the negative ion emission from CaF_2 at steady state was estimated at about 2.81 eV. On the other hand, at the transition state, it was observed that there are several regions with different activation energies, suggesting a possibility that there are several mechanisms with different activation energies (0.51 eV, 1.18 eV and 1.61 eV) in the negative ion emission.

It was also found that the emission current increased with applied voltage.

To clarify the emission mechanism, the applied voltage dependence of the emission current from solid ionic conductors were discussed, by fitting the obtained data using the modified Schottky equation with the multiplying factor α as

$$\log J_{emission} = \log J_0 + \alpha \frac{1.91}{T}\sqrt{\frac{V}{d}} \qquad (1).$$

For example, the fitting result of the applied voltage dependence from YSZ was shown in Fig.3. It can be seen that the modified equation accorded with the data reasonably well in high voltage region, suggesting that

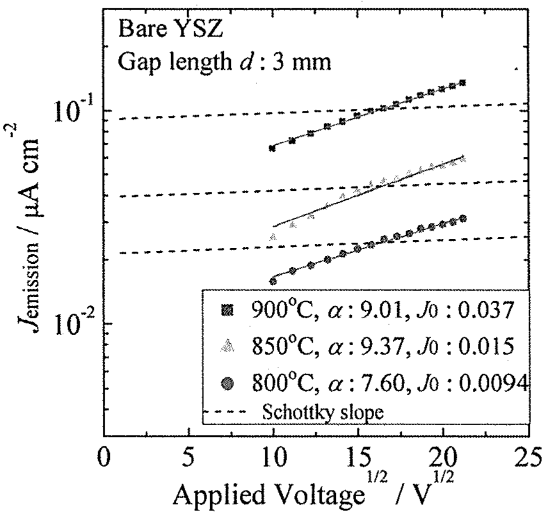

Fig. 3 Fitting of the applied voltage dependence of the emission current from YSZ

the applied voltage dependence is proportional to $\exp(V^{1/2})$ as in the Schottky equation and only its dependence is stronger than that in Schottky equation. This result also implies that the applied voltage dependence is caused by the coulombic interaction similar to that proposed as Schottky effect.

In addition, from the fitting results, two possible reasons were suggested for this Schottky-effect-like mechanism. One is that the actual electric field is α^2 times stronger than that of the apparent one. Another is that the enhancement is caused by the α^2 times stronger attractive force than the image force.

To clarify the real negative ion current from CeO_2, CaF_2 and YSZ, the ratio of negative ions and electrons in the emission current was investigated using time of flight mass spectrometer (TOF-MS) capable of detecting electrons. As a result, the evidence, which indicates the electron emission from the ionic conductors, was not also confirmed from the TOF-mass spectrum of CaF_2, CeO_2 and YSZ.

The ratio from CaF_2 and CeO_2 was also discussed in terms of the decay time constant of the emission current and that of the negative ion counts. In this case, the decay time constants were estimated from the fitting of the decay curves of the emission current and the negative ion counts using the following equation.

$$y = y1 \cdot \exp\left(-\frac{x}{t1}\right) + y2 \cdot \exp\left(-\frac{x}{t2}\right) + y\infty \qquad (2).$$

For example, the decay curve and the fitting result of the emission current and the F^- ion counts from CaF_2 were shown in Fig. 5. It can be seen that the large difference in the obtained decay time constants between the emission current and the F^- ion count was not confirmed. Additionally, in the case of CeO_2, the large difference was not also observed as in the case of CaF_2.

From these results, the strong evidence for the existence of thermal electrons in the emission current was not obtained, and from the obtained decay time constants, it was found that there are several decay processes in the negative ion emission mechanisms.

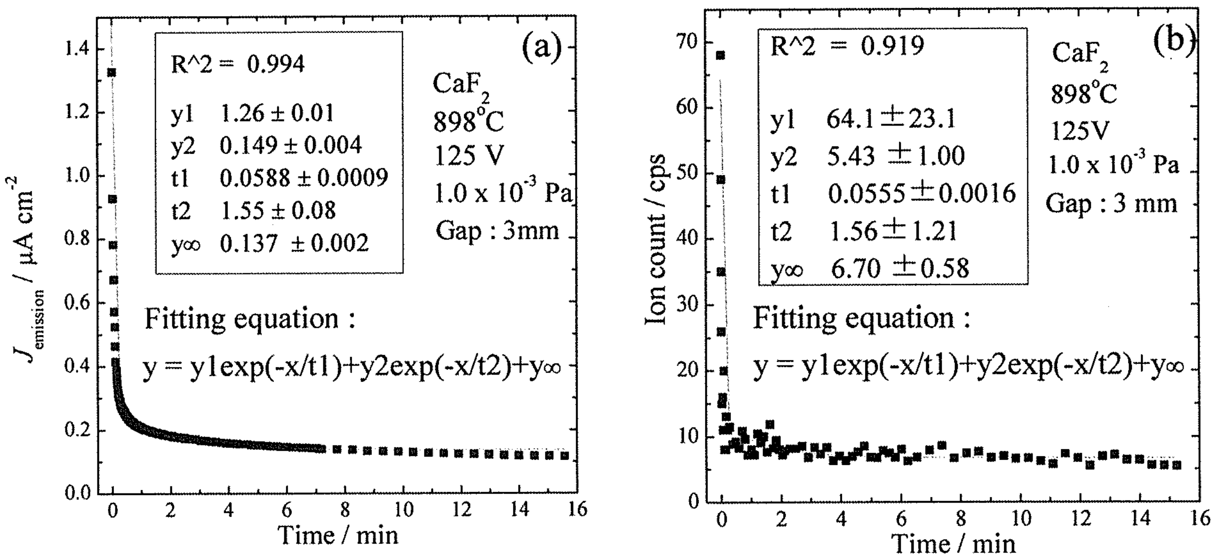

Fig. 4 Decay curve and Fitting result of emission current and F^- ion count from CaF_2 : Emission current (a), F^- ion count (b)

As remarked above, this dissertation proved that it is possible to produce O^- ion beam and to increase the emission current by using CeO_2. This dissertation also proved that this ion beam source can produce the F^- ion beam by using fluoride ionic conductor. Additionally, this dissertation discussed the emission mechanism of this negative ion beam source, and provided the useful information on the clarification of the unrevealed emission mechanism. Finally, it can be concluded that this dissertation greatly contributed to the development of this novel negative ion beam source.

論文審査結果の要旨

最近，イオンビーム工学は材料科学，ナノテクノロジーの基盤技術として特に注目されている。なかでも，その制御の容易さと照射体のチャージアップによる損傷が少ないこと等から，負イオンビームに高い関心が集まっている。東北大学では最近，酸素イオン導電体である安定化ジルコニアに高温で高電圧をかけると一価の酸素イオンビームが放出されるという現象が発見され，ついで東京工業大学などで，アルミン酸カルシウムからも一価の酸素負イオンビームの発生が報告された。本論文はこの一連の現象を取り上げ，その普遍性と原理を探求し，応用への可能性を考察したものであり，全編６章からなる。

第１章は序論であり，本研究の背景となるイオンビーム源の研究概要と，イオン導電性固体がイオンビーム源になることが発見された経緯，および本研究の目的を述べている。

第２章では，酸化セリウムが，安定化ジルコニアを凌ぎ，アルミン酸カルシウムと同等以上のビーム束を与える酸素負イオンビーム源になるという新たな発見と，その温度，電圧依存について述べている。

第３章では，フッ素イオン導電体であるフッ化カルシウムが，フッ素負イオンビーム源となることの新たな発見と，そのビーム源としての特性に関する探求結果について述べている。

第４章は，このイオンビーム発生の原理に関する考察である。エミッション電流は，ショットキー効果から予測される様に，引き出し電圧の平方根の指数関数に比例する。しかし，その電圧依存は理論予測より格段に大きく，実効的な電圧が１０－１０００倍になった状態に相当している。この原因を説明するモデルを考察し，結晶表面のファセットなどによる凹凸がこの原因の一つであろうと推論している。これは負イオンエミッションの電位依存の機構に立ち入った最初の研究である。また，高イオンビーム束を得る方途も示唆しており，工学的にも重要である。

第５章では，飛行時間質量分析法を用いた研究結果を述べている。引き出し電圧に対して発生するビーム電流へのイオンと電子の寄与を分離測定した結果，発生している荷電ビームは全て負イオンによるものであることを初めて明らかにしている。基礎科学・工学の両面から極めて重要な発見である。また，その時間依存からイオンビーム発生機構の考察も進めている。

第６章は，結論である。

以上要するに本論文は，負イオンビームの新しい発生源の発見と，その発生機構解明，工学的応用への可能性の探索を進めたもので，固体イオニクス，ビーム工学，機械システムデザイン工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。